

MONITORING AND EVALUATION OF DUCT EMISSION AND STATIONARY SOURCES OF CERAMIC INDUSTRIES BY SR-TXRF

Silvana Moreira¹, Roney José Fonseca¹, Ana Elisa Sirito de Vives²

¹ Faculdade de Engenharia, Arquitetura e Urbanismo
Universidade Estadual de Campinas
Caixa Postal 6021
13083-852, Campinas, SP
silvana@fec.unicamp.br

² Faculdade de Engenharia, Arquitetura e Urbanismo
Universidade Metodista de Piracicaba
Rodovia Santa Bárbara D'Oeste/Iracemápolis, km 01
13450-000 Santa Bárbara D'Oeste, SP
aesvives@unimep.br

ABSTRACT

The aim of this study was to monitor and evaluate the emission of metals from ducts and stationary sources in ceramic industries in the region of the ceramic centre of Santa Gertrudes in the state of São Paulo. There has been a growth of this industrial sector in recent years. This reflected upon the environment in this region which is responsible for 60% of ceramic tile floor production. From 2005 to 2006, samples of gases emitted by several ceramic companies in that region were collected. Metal concentration was determined through X-ray Fluorescence by Total Reflection with Synchrotron Radiation (SR-TXRF) technique. The analyses were carried out in the National Laboratory of Synchrotron Light (NLSL) and used a polychromatic beam of light to stimulate the samples and a hyper pure Germanic detector for the characteristic X-ray detection. The following elements were detected: Al, S, Cl, K, Ca, Fe, Cr, Mn, Ni, Cu, Zn and Pb. High concentrations of elements such as Chromium, Nickel and Lead were observed in the samples analyzed which presented values of concentrations higher than the ones permitted by legislation.

1. INTRODUCTION

The ceramic industry plays an important role in the country economy with an estimate percentage of 1% in the Gross Domestic Product, which corresponds to approximately 6 billion dollars. The abundance of natural raw materials, alternative sources of energy and availability of technologies helped Brazilian industries to develop quickly and several types of product from several ceramic segments could reach world quality level and export in great quantities [1].

Ceramic industrial sector is quite varied and could be divided into the following segments: red ceramic, covering materials, refracting materials, sanitary ware, artistic ceramics (for decoration and practical use), domestic ceramic water filters, technical ceramics and thermal insulators. Moreover, there are also manufactures of synthetic raw materials for ceramics (calcined alumina, electromelted alumina, silicon carbide and others), of glassy products and dyes, plaster and other chemical products [1].

The constitution of this ceramic center has as its main causes its privileged geographic location (near great consumer centers) as well as the existence of a great line of clayey rocks, with average thickness of 90m and an extension of 200 km approximately. This region is

nested in the so-called Corumbataí formation, which has great extensions of excellent raw material sources for the production of good quality ceramic plates. This raw material does not require the addition of other mineral products, which permits dry industrial process and a production whose cost is much lower than other competitor centers [2].

The abundance of raw material favored an increase in production at low costs and the growing of the companies, which caused a great concentration of industries of all ceramic segments in these regions, associated with the facilities of raw materials, energy, research centers, universities and polytechnic schools [2].

This region, which comprises the Ceramic Center of Santa Gertrudes in the state of São Paulo and embodies the cities of Rio Claro, Limeira, Cordeirópolis and Araras, has 40 ceramic industries and generates 60% of Brazilian glassy floor production. [3]

Despite the present environmental awareness felt by the sector, not before the last decade has the knowledge of its diverse and inherent environmental aspects been developed. One of the most important environment aspects is related to gas emission resultant from high temperatures thermal processes. From all the gas emissions, one of the most worrying is that of the fluoride inorganic compound, resultant from thermal decomposition of raw material. Its greater incidence is in structural ceramic, paving and covering sub-sectors [4-11].

Monitoring and control actions require multielementar quantitative analysis in the level of traces with a great number of samples, considering that maximum permitted levels for metals are generally near $\mu\text{g}\cdot\text{g}^{-1}$. The analytical technique named Total Reflection X-ray Fluorescence (TXRF) presents some advantages in relation to other analytical methods; among those, we could mention mainly the limits of detection which can be found in the proportion of some portions per billion ($\mu\text{g}/\text{mL}$) and its characteristic of being a technique which permits the detection of several elements with only one measure [12].

The aim of this study was to use a technique of Synchrotron Radiation Total Reflection X-ray Fluorescence (TXRF) to identify and quantify metals in order to monitor and evaluate the emission of these elements from ducts and stationary sources of ceramic companies in Santa Gertrudes (SP) region.

2. EXPERIMENTAL

2.1. Characterization of the study area and sampling place

The Ceramic center of Santa Gertrudes comprises approximately eight cities, among which there are the cities of Rio Claro, Limeira, Cordeirópolis, Piracicaba and Santa Gertrudes, where there are presently approximately 40 ceramic companies. Fifteen companies were sampled in 2005 and thirteen in 2006 (Table 1).

Table 1. Sample Dates and Study Areas in 2005.

Code	City	Year 2005	Year 2006
A	Sumaré	Jun, 28	Jun, 08
D	Rio Claro	Jun, 29	Jan,13/Jun, 01/Jul, 22
E	Rio Claro	_____	May, 31/Jul, 08
F	Limeira	Jan, 14	Aug, 11
G	Cordeirópolis	May, 27	-----
H	Limeira	Nov, 10	Feb, 08/Apr, 14
I	Santa Gertrudes	Jan, 04	-----
J	Rio Claro	Feb, 28	Mar, 08
K	Santa Gertrudes	Aug, 31/Oct, 22	Feb,06
L	Cordeirópolis	Aug, 31/Sep, 13	_____
M	Santa Gertrudes	Set, 02	Jul,17
N	Mogi Guaçu	Jan, 27	-----
O	Cordeirópolis	Sep, 14	-----
P	Cordeirópolis	Sep, 06	-----
Q	Santa Gertrudes	Nov, 04	Feb, 06/Mar, 03
R	Cordeirópolis	Oct, 15	
S	Cordeirópolis	-----	Mar, 28
T	Santa Gertrudes	-----	Mar, 30
U	Santa Gertrudes	-----	Mar, 06
V	Piracicaba	-----	Jan, 09

2.2. Sampling method

Samples were collected from 2005-2006 following the norms for samples proposed by CETESB. The norms applied were: L9.210 (Oct/90) – Combustion Analyses with ORSAT device; L9.213 (Sept/95) – Ducts and Stationary Sources (Determination of Fluoride through the method of specific ion electrode); L9.221 (Jul/90) – Ducts and Chimneys of Stationary Sources (Determination of Sampling Points); L9.222 (May/92) – Ducts and Chimneys of Stationary Sources (Determination of Velocity and Gas Leak); L9.223 (Jun/92) – Ducts and Chimneys of Stationary Sources (Determination of Dry Molecular Mass and of excess of Air in Gas Flux); L9.224 (Aug/93) – Ducts and Chimneys of Stationary Sources (Determination of Humidity of Effluents); E16.030 (Aug/93) – Ducts and Chimneys of Stationary Sources (Calibration of equipment used in gas effluent sampling) [13 – 21]. A scheme of the sampling system was showed in the Figure 1 while in the Figure 2 can be observed the equipment used for register information as: collected gas volume, in and out temperature and gas pressure. Figure 3 shows a sampling in course.

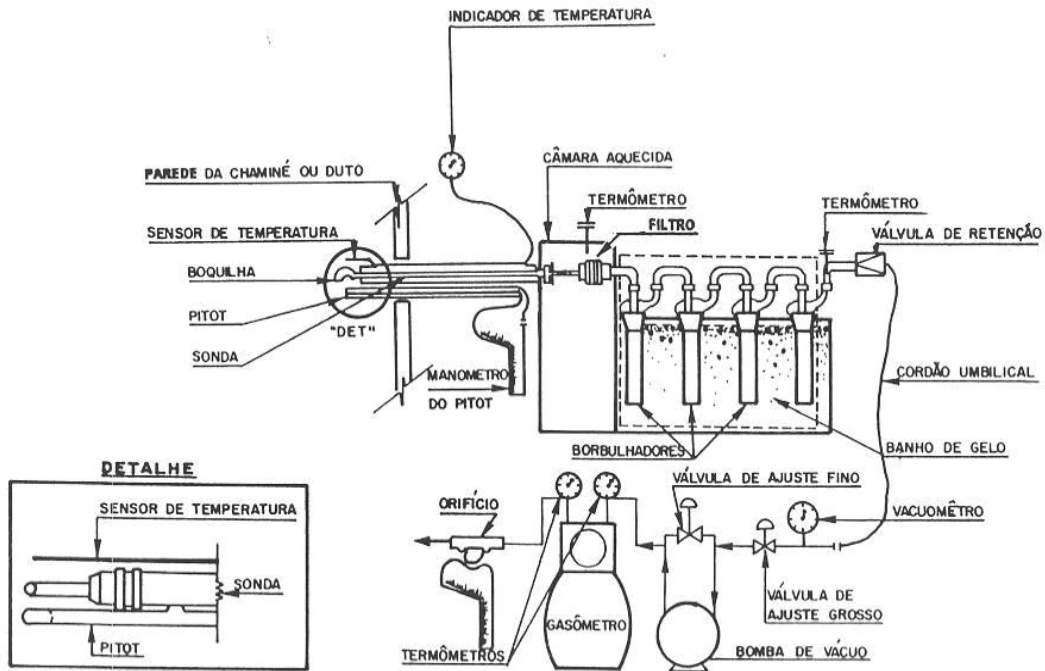


Figure 1. Illustration of the equipment used for duct sampling in stationary sources.



Figure 2. System applied in atmospheric emission sampling.



Figure 3. Sampling in course.

2.3. Measures and samples preparation

For the SR-TXRF analysis, an aliquot of 1 mL was obtained from each sample. The samples were then transferred to Eppendorff tubes and received an addition of 100 μL of a Ga solution (102.5 mg.L^{-1}) as internal standard. Then, the mixture was homogenized and 5 μL were putted onto the surface (Lucite or Perspex). Finally, the sample deposited on the sample holder was left to dry under an infra-red light. The samples were prepared triplicate.

The samples were analyzed in the Synchrotron Light Source Laboratory (LNLS) in Campinas, in the X-ray Florescence beamline (D09B) under total reflection conditions. The samples were measured by 100 seconds using a polychromatic beam and the characteristic X-rays were detected with a semi-conductor Ge hyper-pure detector with a resolution of 150 eV for the energy of 5.9 keV [22].

2.4. System calibration and quantitative analysis

In SR-TXRF, there is no occurrence of absorption and enhancement effects so there is no need for the correction of matrix effect and, thus, the fluorescent intensity of element i is directly proportional to its concentration (Equation 1).

$$I_i = S_i C_i \quad (1)$$

in which:

I_i = liquid intensity of X-rays of characteristic line K or L of i element of interest (cps/ppm);
 S_i = elementar sensitivity of the system for element i (cps.mL/ μg); C_i = concentration of element i in the pipetted solution on the holder sample ($\mu\text{g/mL}$).

In order to correct the instabilities of the system, such as fluctuations of synchrotron radiation beam, detection of X-rays and operational errors, such as pipetting or positioning of samples, etc an internal standard was added to the samples. The elements to be used as internal standards must be the ones which are not present in the samples and, thus, elements as Ge and Ga have been used most often for environmental samples, and Co and Y for other types of samples.

Using equation 1, one can determine the ratio between the intensity of element i and the internal standard y (equation 2).

$$\frac{I_i}{I_y} = \frac{s_i C_i}{s_y C_y} \quad (2)$$

in which:

I_i = liquid intensity of the element i in the sample (cps); I_y = liquid intensity of the internal standard y (cps); s_y = detector sensitivity for internal standard y (cps.mL/ μ g); s_i = detector sensitivity for the element i (cps.mL/ μ g); C_i = concentration of element i of interest (μ g/mL); C_y = concentration of internal standard y in the sample (μ g/mL).

Resulting in:

$$S_{Ri} = \frac{S_y}{S_i} \quad (3)$$

Replacing equation 3 in equation 2, one will obtain the equation used to calculate the concentration of the element of interest (equation 4).

$$C_i = \frac{I_i}{I_y} S_{Ri} C_y \quad (4)$$

in which:

S_{Ri} = relative sensitivity for the element i in relation to the internal standard y (non-dimensional).

To determine the concentration of elements of interest it is necessary to determine the relative sensitivities. Thus, multi-elementary standard solutions in different concentrations, containing Al, Si, K, Ca, Ti, Cr, Fe, Ni, Zn, Ga, Se, Sr and Mo for the K series and Mo, Cd, Ba, Sb, Pt, Tl and Pb for the L series were prepared by dilution of stock solutions. Gallium was added by following the same procedures adopted in the sample preparation.

A relation between the relative sensitivity for an element present in the multi-elementary standard solution and the atomic number may be obtained. Then, one can interpolate the sensitivity for other elements detected in the samples and which are not present in the standard solution, thus, consequently, one can estimate its concentration in the sample of interest. Similarly, the same equations may be used for the K_{β} line, as L and M, in which the relative sensitivities will have, of course, other values [23].

3. RESULTS AND DISCUSSION

3.1. System calibration

The adjustment of X-rays characteristic spectra in order to obtain the fluorescent intensities were carried out through the AXIL program (*Analysis of X-ray spectra by Interactive Least squares fitting*), which integrates the computational package QXAS (*Quantitative X-ray*

Analysis System), developed by the University of Antwerp, Belgium, and provided by the International Atomic Energy Agency (IAEA).

After the determination of the experimental relative sensibilities, the points were adjusted in order to perform the relationship between the relative sensitivity and the atomic number. So the curves for K (Equation 5) and L (Equation 6) series were obtained.

$$S_R = \exp(19.14179 + 1.25078Z - 0.02044Z^2) \quad (5)$$

$$R^2 = 0.99421$$

$$S_R = \exp(-20.54286 + 0.36209Z - 0.00109Z^2 - 3.235310^{-5}Z^3) \quad (6)$$

$$R^2 = 0.99502$$

3.2. Procedure validation for quantitative analysis by SR-TXRF.

In order to validate the method, two reference samples were analyzed, prepared like the unknown composition samples (Tables 2 and 3).

Table 2. Measured and Certified Values for Drinking Water Pollutants.

Element	Measured Value (mg.L ⁻¹)	Certified Value (mg.L ⁻¹)
Cr	9.21 ± 0.18	9.09 ± 0.45
As	8.46 ± 0.17	9.09 ± 0.45
Se	4.26 ± 0.07	4.54 ± 0.23
Cd	4.74 ± 0.64	4.54 ± 0.23
Ba	83.23 ± 0.76	90.91 ± 4.55
Pb	9.77 ± 1.01	9.09 ± 0.45

Table 3. Measured and Certified Values for Trace Elements in Natural Water (NIST/SRM 1640).

Element	Measured Value (µg.kg ⁻¹)	Certified Value (µg.kg ⁻¹)
Ca*	6.34 ± 0.03*	6.40 ± 0.08*
K	825.24 ± 7.18	903.64 ± 24.00
V	11.78 ± 2.07	11.81 ± 0.33
Cr	36.17 ± 0.85	35.09 ± 0.91
Mn	99.66 ± 5.63	110.45 ± 1.00
Co	15.67 ± 0.74	18.44 ± 0.28
Ni	18.89 ± 1.5	24.9 1± 0.73
Cu	68.93 ± 1.68	77.45 ± 1.09
Zn	49.85 ± 0.96	48.36 ± 0.91
Rb	21.11 ± 0.88	19.96 ± 0.20
Sr	102.72 ± 5.51	112.91 ± 0.64

*in mg.kg⁻¹

The measured values showed relative standard deviation lower than 9% for most elements, indicating good adjustment in the calibration curve.

3.3. Quantitative analysis – determining metal concentrations

After the determination of the sensitivity, the elemental concentrations present in the samples were determined and the results are shown in Tables 4 and 5.

Table 4. Al, S, Cl, K, Ca and Fe concentrations (mg/Nm³) determined by SR-TXRF.

Company	Al	S	Cl	K	Ca	Fe
H	85 ± 14	106 ± 9	18 ± 1	8 ± 2	18 ± 2	13 ± 1
T	453 ± 55	178 ± 14	52 ± 29	19 ± 5	26 ± 2	77 ± 15
Q	360 ± 28	85 ± 3	72 ± 1	15 ± 8	26 ± 4	10 ± 4
D	316 ± 4	95 ± 1	14 ± 2	11 ± 4	17 ± 2	6 ± 2
D	216 ± 20	121 ± 7	10 ± 1	4 ± 1	16 ± 6	13 ± 6
K	316 ± 21	139 ± 34	20 ± 4	12 ± 5	17 ± 2	11 ± 6
K	205 ± 33	139 ± 15	14 ± 8	12 ± 5	24 ± 5	5 ± 1
M	384 ± 7	231 ± 30	21 ± 1	9 ± 1	16 ± 1	43 ± 3
G	703 ± 25	617 ± 3	90 ± 6	15 ± 8	24 ± 5	212 ± 8
F	759 ± 13	201 ± 11	77 ± 18	13 ± 1	85 ± 4	55 ± 8

Table 5. Cr, Mn, Ni, Cu, Zn and Pb concentrations (mg/Nm³) determined by SR-TXRF.

Company	Cr	Mn	Ni	Cu	Zn	Pb
H	3.44 ± 0.52	0.74 ± 0.09	3.27 ± 1.13	0.23 ± 0.01	0.62 ± 0.12	0.05 ± 0.02
T	18.34 ± 4.25	0.59 ± 0.05	7.93 ± 0.02	0.56 ± 0.22	2.27 ± 0.12	0.10 ± 0.04
Q	2.10 ± 0.47	0.24 ± 0.02	1.89 ± 0.51	0.70 ± 0.03	2.92 ± 0.53	0.16 ± 0.05
D	1.11 ± 0.34	0.08 ± 0.01	0.75 ± 0.38	0.11 ± 0.01	0.44 ± 0.05	0.03 ± 0.01
D	2.29 ± 0.28	0.15 ± 0.03	1.24 ± 0.22	0.17 ± 0.04	0.83 ± 0.08	0.09 ± 0.01
K	2.12 ± 0.60	0.37 ± 0.08	2.17 ± 0.39	0.24 ± 0.03	1.39 ± 0.09	0.13 ± 0.03
K	1.10 ± 0.07	0.56 ± 0.10	1.57 ± 0.71	0.17 ± 0.03	1.61 ± 0.07	0.16 ± 0.01
M	10.44 ± 0.48	0.35 ± 0.03	4.69 ± 0.20	0.43 ± 0.12	0.89 ± 0.05	0.18 ± 0.05
G	36.76 ± 1.09	3.45 ± 0.71	19.40 ± 2.97	0.41 ± 0.05	3.90 ± 0.61	0.47 ± 0.04
F	23.26 ± 2.08	2.70 ± 0.21	16.02 ± 1.08	0.94 ± 0.12	2.45 ± 0.61	1.42 ± 0.08

After the spectra adjustment of the samples, the background (area below the characteristic peak of each element) intensities were obtained and the minimum detection limits (MDL) were set. Values ranged from 440 µg/Nm³ for Aluminum to 0.077 µg/Nm³ for Zinc, and were below the values established by legislation.

Currently in Brazil, there are not many norms concerning atmospheric emissions which establish concentration limits or emission rates of pollutants. Today, only some resolutions are in vigor such as CONAMA 382/2006 (which establishes emission criteria for boilers only), CONAMA 264/1999, (exclusive for emission patterns of heavy metals for co-processing ovens) and SEMA 54/2006 (Resolution, which establishes norms for the state of Paraná only) [24-26].

We have used in this study a comparison of results with CONAMA 264/99 (Table 6). The emission patterns are specific for some metals such as Mercury, Lead, Cadmium and Thallium and for other grouped metals.

Table 6. Emission limits for co-processing ovens.

Pollutant	CONAMA*	SEMA**
Hg	0.05 mg/Nm ³	0.05 mg/Nm ³
Pb	0.35 mg/Nm ³	0.35 mg/Nm ³
Cd	0.10 mg/Nm ³	0.10 mg/Nm ³
Tl	0.10 mg/Nm ³	0.10 mg/Nm ³
As+Be+Co+Ni+Se+Te	1.4 mg/Nm ³	-
As+Be+Co+Cr+Cu+Mn+Ni +Pb+Sb+Se+Sn+Te+Zn	7.0 mg/Nm ³	7.0 mg/Nm ³
As+Co+Ni+Se+Te+Be	-	1.4 mg/Nm ³

(*)CONAMA 264/99 Resolution – values specified at 10% O₂, dry base.

(**)SEMA 54/06 Resolution – values specified at 7% O₂, dry base.

Figure 4 shows the variation of Pb concentration in several companies sampled. In accordance with CONAMA 264/99 resolution, which establishes the maximum emission limits (MEL) for heavy metals for residue burning in co-processing ovens, the maximum value allowed for this element is 0.35 mg/Nm³. The maximum emission limit allowed by CONAMA 264/99 resolution was not complied with by two ceramic industries (G and F).

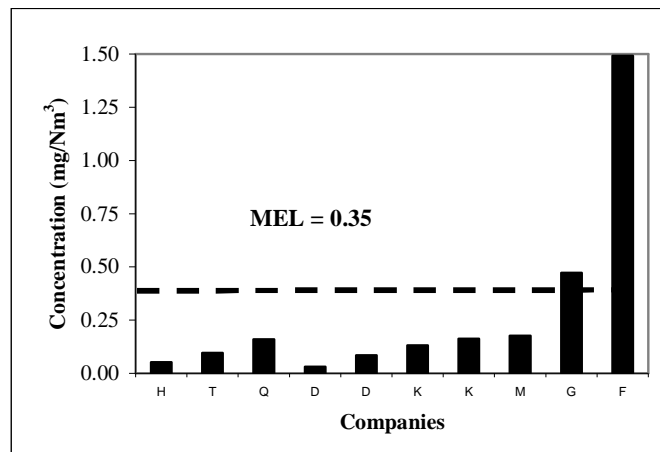


Figure 4. Lead concentrations determined by SR-TXRF in the ceramic industries sampled in 2005 and 2006.

Still in accordance with the same resolution, the sum of element concentrations (As, Be, Co, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sn, Te, Zn) should not exceed 7.0 mg/Nm^3 , as maximum emission limits. Figure 5 shows the sum of Cr, Mn, Ni, Cu, Zn and Pb. It can be observed that six (06) out of the ten (10) industries analyzed showed values higher than those established by legislation, suggesting that most ceramic companies throw several metals in the atmosphere in numbers higher than those found in co-processing companies, which use residues to burn and manufacture cement.

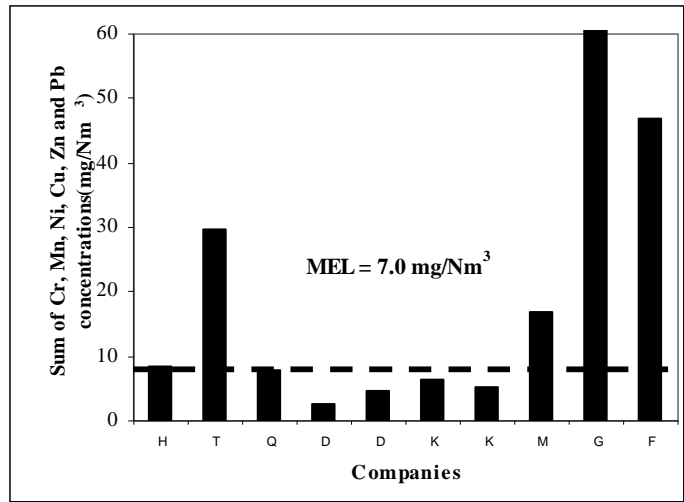


Figure 5. Sum of Cr, Mn, Ni, Cu, Zn and Pb concentrations, compared to the sum value established by CONAMA 264/99 legislation.

Chromium and Nickel concentrations values were higher than those established by legislation, as observed in Figure 6. Chromium concentrations for companies T, M, G and F are much higher than the maximum emission values.

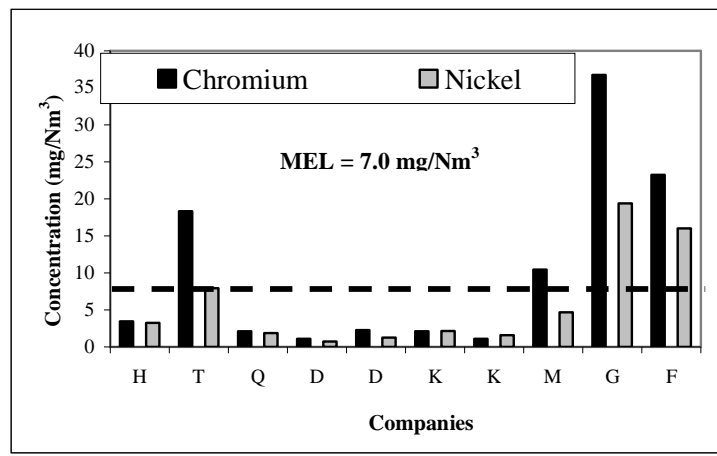


Figure 6. Chromium and Nickel concentrations determined by SR-TXRF in ceramic industries sampled in 2005 and 2006.

Combustion of fuels in stationary sources was the main emission source for As, Cd, Cr, and Ni (more than a half of the total anthropogenic emissions), while combustion of gasoline was the main source of for lead. There is a continuous reduction of heavy metal emissions in Europe during the last 40 years. Better knowledge of heavy metal sources, emissions, pathways, and fate in the environment and progress in developing efficient emission control equipment has resulted in more efficient regulatory efforts to curb heavy metal emissions from anthropogenic sources very substantially. There is a potential for further reduction of these emissions until the year 2010 up to about 40% for As, Cd, Cr, and Ni and about 57% for Pb [27].

The characteristics of particulate matter (PM) emission such as the estimation of emission factors, size distributions and of heavy metal emission from small-size incinerators and boilers have been investigated. The emission ratios of PM-10 to TPM (total PM) from boilers and incinerators ranged from 29% to 62% and 10% to 84%, respectively, which resulted in more and larger sized PM emission due to poorer combustion from solid waste incinerators than boilers. Cadmium, copper, lead and zinc on the fine PM under 2.5 μm accounted for approximately 90% of the total mass of each metal in PM-10 [28].

In Rio de Janeiro city a study shows that the contribution of stationary sources is majority in relation two parameters: inhaled particulate matter and sulfur dioxide, 58% and 88%, respectively. The information obtained by the inventory indicates that mobile sources were responsible for 77% of the total pollutants emitted in the atmosphere and stationary sources, 33% [29].

According to CETESB in Santa Gertrudes (Jardim Luciana) was observed the occurrence of episodes of inadequate and bad air quality in 2008. The maximum daily concentrations exceeded the daily standard of inhaled particles ($150 \mu\text{g}/\text{m}^3$) in Santa Gertrudes (Jardim Luciana) eight times and one day surpassed also the attention level ($250 \mu\text{g}/\text{m}^3$). The annual average of inhaled particles in 2008 was $97 \mu\text{g}/\text{m}^3$, exceeding the annual standard ($50 \mu\text{g}/\text{m}^3$). In Santa Gertrudes city are installed several industries of ceramic pavements, which activities are the potential sources of particulate material into the atmosphere. The emissions of particulate matter by the main three industries of Santa Gertrudes in 2008 were 0.10, 0.13 and 0.08 ton/year [30].

The study in order to identify the contribution of the emissions of the ceramics industries to the atmospheric particulate that is susceptible to depositing on vegetation and accumulating in the substratum was presented by Sanfeliu *et al*, [31]. Samples obtained from high volume collectors were studied. Two zones were considered: zone A, a high volume collector located in the municipalities adjacent to the companies that were the object of the study; and zone B, a high volume collector further away from the said companies and adjacent to a power station and a refinery. The results obtained in the chemical analysis demonstrate that (a) the influence of the frits and enamel production on the high concentrations of Zr, Cu and Ce obtained in zone type A compared with zone B; (b) the affect of clays used as raw materials in the ceramics industry can be demonstrated by the high concentrations of Fe, Al and Mg. The weekly evolution showed two series of elements, a characteristic group of dust emissions and another group of tracers from high temperature processes

4. CONCLUSIONS

A major concern found throughout this investigation was to verify that several toxic elements such as Chromium, Nickel and Lead are emitted by stationary sources from several companies that were monitored.

It was verified that 60% of the industries investigated presented values for the sum of Cr, Mn, Cu, Zn and Pb concentrations above the values established by CONAMA legislation, indicating that most ceramic companies throw several metals in the atmosphere in concentrations above than those found in co-processing companies, which use residues to burn and manufacture cement.

Cr, Ni and Pb concentrations were higher than those allowed for cement companies (whose sector is potentially more pollutant than the china). Thus, the environmental issue in the region of Santa Gertrudes, where occurrence of problems concerning fluoride emission is seen already, may be related to the presence of these highly toxic elements

ACKNOWLEDGMENTS

The authors thank the Synchrotron Light Source Laboratory (LNLS) for carrying out the measurements (Project XRF 5702), the Bioagri Environment Laboratory for assistance with samplings and CNPq (Processes 308432/2007 e 474007/2007).

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